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Specification and Drawings, as originally filed, with Application for Patent Serial No:
2,,250,628, on October 13, 1998, by **SELECT MOLECULAR TECHNOLOGIES**
CORPORATION, assignee of Dmitry N. Borisenko and Nikolay N. Borisenko, for "High
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ABSTRACT

A high capacitance energy storage device where electrodes are formed of layers of a carbonised, activated woven fabric that has been impregnated with an electrolyte.

5 The electrolyte is absorbed by active centers at the surface of the carbonised, activated material. The prepared fabric is sandwiched between alternating graphite-based separators and non-conductive membranes to form a capacitor structure exhibiting very high capacitance, non-degradation over multiple charging/discharging cycles, and, in AC
10 installations, reliable and reproducible characteristics. In addition, the materials in the device are environmentally friendly.

HIGH CAPACITANCE ENERGY STORAGE DEVICE**Field of the Invention**

5 The present invention relates to energy storage devices. In particular, the present invention relates to high capacitance energy storage devices, such as capacitors.

Background of the Invention

10 Relatively inexpensive and reusable electrical energy storage devices are clearly desirable. Prior art storage devices mainly consist of electrochemical cells. Typical electrochemical cells or batteries, such as iron-nickel and nickel-cadmium cells, have a number of well known disadvantages. Generally, the substances used to produce such cells are expensive and relatively scarce. These substances also tend to be non-recyclable, and
15 potentially harmful to the environment, resulting in both costly production, reclamation and disposal. Electrochemical cells have a limited service life, ie. number of charge/discharge cycles, and shelf life, due to the irreversible reaction of either the electrolyte or electrodes in every charge/discharge cycle. In addition, their efficiency is relatively low, typically in the range of 15 - 50%, and depends on the operating conditions in which they are used, such as
20 the ambient temperature.

 Some advances have been made in the field of electrochemical batteries, such as the suppression of gas evolution by adding variable valency compounds to the electrolyte, and replacing environmentally harmful substances with metal hydrides. However, these
25 advances add considerably to the cost of producing batteries and have not been widely adopted. Furthermore, the primary disadvantages of conventional batteries, their low efficiency, limited lifespan and degrading output, are not greatly improved by these changes.

 Capacitors capable of storing large amounts of electrical energy, such as
30 carbon double layer capacitors, are also known. Typically, these capacitors use carbonised materials to form polarized electrodes. Generally, the carbonised material is a paste formed

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from a carbon particle powder in combination with a binding agent. The carbon paste is spread over a metallic mesh which is packaged in a housing at high pressure to form the electrodes. While such capacitors have a theoretically high capacitance, the paste used exhibits non-Newtonian flow characteristics, and, therefore, under the high pressures required to achieve good electrical properties, the symmetric geometry of the electrodes necessary to produce high capacitance is compromised. Changes in the electrode geometry lead to variations in the electric characteristics of separate cells, which fact leads to the destabilization of the capacitor in general and its eventual breakdown.

Summary of the Invention

It is an object of the present invention to provide a high capacitance energy storage device that overcomes the disadvantages of the prior art.

In a preferred embodiment, there is provided a high capacitance energy storage device, comprising:

a housing electrically isolated from, and lined with, conductive, chemically inert separators, said separators electrically connected to contacts mounted on said housing;

at least one capacitive cell having a first electrode separated from a second electrode by a non-conductive, chemically inert membrane, said electrodes formed of a carbonised and activated woven fabric impregnated with an electrolyte, said cell being in electrical and mechanical contact with said separators;

wherein said membrane permits free passage of molecules of said electrolyte therethrough.

In a further aspect, there is provided a capacitive cell for a high energy storage device, comprising:

a first electrode separated from a second electrode by a non-conductive, chemically inert membrane, said electrodes formed of a carbonised, activated woven fabric impregnated with an electrolyte, said chemically inert membrane permitting free passage of molecules of said electrolyte therethrough.

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Brief Description of the Drawings

Preferred embodiments of the present invention will now be described, by way of example only, with reference to the attached Figures, in which:

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Fig. 1 shows a cross section of a single layer cell of a high capacitance energy storage device according to the present invention;

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Fig. 2 shows a cross section of a double layer cell of a high capacitance energy storage device according to the present invention;

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Fig. 3 shows a cross section of a high capacitance energy storage device having a two double layer cells connected in series, according to the present invention; and

Fig. 4 shows a graphical representation of current density in relation to applied sandwiching pressure for a high capacitance energy storage device according to the present invention.

Detailed Description

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A first embodiment of a high capacitance energy storage device 10 according to the present invention is shown in Fig. 1. Device 10 consists of a housing 12 within which a single layer capacitive cell 14 is contained. In a preferred embodiment, housing 12 is a duralumin shell separated from cell 14 by current collectors 16, 18 which electrically isolate the housing 12 from the cell 14. Current collectors 16, 18, shown in Fig. 1 as separate elements, can form part of housing 12. If current collectors 16, 18 form the upper and lower surfaces of the housing 12, the side walls are chosen to electrically isolate them from each other. In this case, the side walls can be an appropriate dielectric material. The case is air tight and its internal surface is chemically isolated from an electrolyte used in the cell.

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Contacts (not shown) are provided on the exterior of the housing 12, as is well known to those of skill in the art.

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Cell 14 consists of electrodes 20, 22 separated by a non-conductive, chemically inert membrane 24. The non-conductive, chemically inert membrane can be chosen from a wide selection of materials, provided they are transparent to the electrolyte particles. Suitable materials include: mipor, miplast, cellulose or paper-based sheets, and perforated polymer films, such as polyethylene, polystyrene and fluoroplast. The membrane 24 is transparent to the molecules of the electrolyte to permit the free passage of the molecules therethrough under the influence of an applied voltage. In a currently preferred embodiment, sulphuric acid has been found to be a suitable electrolyte, but the present inventors contemplate that other electrolytes, as are known to those skilled in the art, can be employed. Generally, any electrolytic liquid, whose molecules initially have a non-uniform electron density, is applicable. It has been found that if the electrolyte is ionic, the effect of the charge redistribution at the time of charging device 10 is be more efficient.

Conductive, chemically inert separators 26, 28, that are barriers to the electrolyte molecules, are inserted between the housing 12 and the electrodes 20, 22 to chemically isolate the cell 14 from housing 12. The separators 26, 28 can be formed from a variety of materials have a graphite base. Such chemically inert materials include: graphite plates and graphite foil (graphlex), conductive rubber and conductive polymer films..

Electrodes 20, 22 are made of a regularly structured organic substance, such as material woven from hydrocellulose. The hydrocellulose material is carbonised, and activated, or charged. Suitable woven materials are presently available for use as charged filters and, in the medical field, to cover wounds. Carbonisation is conducted for the purpose of producing chemically inert materials from the organic substance. Activation creates a porous structure with active centres. A method of producing such materials is described in Russian Federation Patent No. 2000360, dated January 22, 1992. In a currently preferred embodiment, the inventors of the present invention have successfully employed UVIS-AC cloth, manufactured by UVICOM, but other similar materials can be used as well. Generally, the carbonised, activated material should exhibit a specific surface area of 800 - 2000 m²/g, a total porosity of 0.25 - 0.80 cm³/g, and surface density of 100- 300 g/m², and should contain little or no ash.

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In a preferred embodiment, the electrodes 20, 22 are made of a woven fabric with a regular structure. The fabric is carbonised and activated, as described above. An electrolyte, such as sulphuric acid in solution, is impregnated onto the carbonised activated electrode fabric. The electrolyte can be any liquid, the molecules of which will have a non-uniform electron density when absorbed into the active centers on the carbonised, activated fabric, or when an electric field is applied. The impregnation of the electrolyte is a purely physical absorption. A free volume of the electrolyte is absent once absorbed. The electrolyte is mainly absorbed on the electrodes and the non conductive inert transparent membrane. The electrolyte is a solution, mixture or a pure substance, particles of which at the time of supplying the electrodes with a difference of potentials, can transfer into a new energetic condition by means of moving ions of disassociated molecules, disassociation, putting into order, orientation, deformation, solvation and dissolvation, adsorption and desorption, shifting of the balance of reversible reactions, complex creation, etc.; the above mentioned phenomena and the electrolyte can be, in particular, assisted by the electrodes possessing active centres, in particular, carbonyl, carboxyl, hydroxyl and other groups. Generally, the impregnated electrodes exhibit characteristics of a solid body, as opposed to a non-Newtonian fluid as in the prior art.

The device 10 is assembled as describe above while ensuring that the electrode geometry is regular. The electrode geometry at the time of assembly is confirmed by ensuring a dependence between the received current density J relative to the pressure applied at the time of assembly, as shown in Fig. 4. As Fig. 4 shows, at pressures greater than 40 psi, further increase in pressure does not significantly alter the current density. In a preferred embodiment, device 10 is assembled at pressure of about 30 to about 80 psi. It has been found that this pressure range is sufficient to ensure reliable contact of all parts and elements contained in the capacitor. ~~In comparison with the high pressures required in prior art capacitors, this lower pressure of assembly can substantially simplify manufacture.~~

As will be apparent, the absorption of the electrolyte into the carbonised, activated woven fabric forms a generally solid, chemically indifferent electrode/electrolyte interface. At the very surface of the electrodes there is, in fact, a two phase, ie. solid/liquid

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surface. This has the advantage of dispensing with electrochemical reactions between the electrodes and electrolyte during charging and discharging, as is found in prior art high capacitance capacitors and batteries. It is believed that the absence of electrochemical reactions at the interface results from the low voltage at which device 10 can operate. The nominal operating voltage for device 10 is less than that which causes a reaction to occur. For example, if the disassociation voltage for water is 1.24 V, then device 10 is operated at a voltage below 1.24 V to prevent disassociation.

The behaviours of the electrolyte particles near an electrode surface can be approximated by double layer capacitance theory. In double layer capacitors, a double layer is formed on the electrode surface by applying an electric field across the electrodes such that the electrolyte is absorbed by the electrode. Each electrolyte particle can be modelled as an elementary capacitor, with a capacitance, in Farads, of:

$$C = \frac{\epsilon_0 \epsilon S}{d}$$

where $\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$

$\epsilon =$ permittivity of free space ≈ 1 (assuming interparticle space between electrolyte ions to be a vacuum)

$S =$ electrode surface area (m^2)

$d =$ distance between an electrode surface and the center of an electron density of the electrolyte particle

Assuming the radius of an electrolyte particle to be in the order of $0.3 \times 10^{-10} \text{ m}$, the capacitance per unit area can be approximated as:

$$C' = \frac{C}{S} \approx \frac{\epsilon_0}{d} \approx 0.3 \text{ F/m}^2$$

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Typically, an impregnated, woven fabric as described above has an electrode surface area in the range of 1000 m²/g, and as high as 2500 m²/g, resulting in energy storage devices having capacitances in the range of 300 - 750 F/g.

5 The energy stored by device 10 can be calculated by determining:

$$W = \frac{C U^2}{2}$$

10 where U = the voltage applied across the electrodes.

Fig. 2 shows a second embodiment of a high capacitance energy storage device 30, having a double layer capacitive cell 34, in accordance with the present invention. Similar elements are referenced by similar numerals in all Figures. Cell 34 consists of two
15 electrodes 40, 42. Each electrode 40, 42 consists of two layers 44, 46 of the impregnated, woven material described above, thereby effectively doubling the capacitance, as will be well understood to those familiar with capacitor design, of the resulting device 30 in comparison to the embodiment of device 10.

20 Fig. 3 shows a third embodiment of a high capacitance energy storage device 50 having two cells 34 connected in series within housing 12. As will be well understood by those skilled in basic circuit theory, connecting the cells in series doubles the voltage that can be applied across device 50 as the device 30.

25 As an example of a high capacitance energy storage device according to the present invention, the inventors of the present invention have constructed a high capacitance energy storage device consisting of three 2 V units, each unit consisting of a pair of cells connected in series, as shown in Fig. 3. The device was built to resemble the standard case of a 6V chemical battery, IEC4R25. Each unit has dimensions 62x62x30 mm, giving a volume
30 of 110 cm³ and a mass of 105 gm. The electrodes of each cell are formed of 18 layers of the carbon impregnated woven material, such that each 2V unit consists of 72 layers of the

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carbonised activated material, and the total electrode volume is 43 cm³ (44x44x22 mm) with a mass of 95 gm.

5 The device was charged over an extended period, until the charging current was less than 1mA. Once charged, each of the three capacitive cells exhibited a capacitance of 700 F±10%, supplying an energy equal to 1400 J, at 2V. The electrolyte chosen consisted of sulphuric acid in a water solution. The specific energy, excluding the mass and volume of the housing, for the device was 32 J/cm³ or 15 J/gm, with an effective output, including the mass and volume of the housing, measured at 12 J/cm³ or 7 J/gm.

10 This device has been observed by the inventors to function for three years without interruption as a solar battery in a pulsed operation under natural conditions. No deterioration of characteristics was noticed over that period.

15 The device of the present invention has significant advantages over prior art energy storage devices. Manufacture of devices from an impregnated woven fabric regular, reproducible and constant characteristics permits reproduction of capacitors with identical characteristics which do not change with time. The energy storage device of the present invention does not degrade over time, nor do its characteristics change over numerous
20 charging/discharging cycles. Reliable, regular and reproducible contact between the electrode surface, the conductive, inert, non-transparent separator, and with the surface of the non conductive inert transparent membrane particularly decreases the internal resistance. of the device in comparison with the prior art.

25 Adding additional layers of fabric to the electrodes and linking cells in parallel and series permits the production of energy storage devices with a variety of nearly unlimited capacitances, voltage and current characteristics. As a result, within the same housing cells can be arranged in series and/or parallel, with the only addition being the provision of further separators.

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The device of the present invention can also be used in AC installations without any risk of explosion or failure, since it shares the characteristics of a non-electrolytic bipolar capacitor, though it exhibits significantly higher capacitance, and significantly lower self-discharge.

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All the materials used in the manufacture of the device of the present invention that come in contact with the electrolyte are chemically inert and do not contain metals. This means that irreversible chemical reactions that cause electrolyte degradation in prior art capacitors, such as gas emission, and the formation of insoluble substances, do not occur in the devices of the present invention. in fact, during the process of charging or discharging, no electro chemical processes take place.

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The resulting energy storage device is bipolar. In other words, if charged with one polarity it can be completely discharged and charged with the opposite polarity without risk of explosion or failure. In addition, short circuiting the device does not damage it.

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It will be apparent to those skilled in the art that the foregoing is by way of example only. Modifications, variations and alterations may be made to the described embodiments without departing from the scope of the invention which is defined solely in the claims.

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We claim:

1. A high capacitance energy storage device, comprising:
a housing electrically isolated from, and lined with, conductive, chemically
5 inert separators, said separators electrically connected to contacts mounted on said housing;
at least one capacitive cell having a first electrode separated from a second
electrode by a non-conductive, chemically inert membrane, said electrodes formed of a
carbonised and activated woven fabric impregnated with an electrolyte, said cell being in
electrical and mechanical contact with said separators;
10 wherein said membrane permits free passage of molecules of said electrolyte
therethrough.
 2. A device according to claim 1, wherein said separators consist of a graphite-
based material.
15
 3. A device according to claim 2, wherein said separators consist of graphite
sheets.
 4. A device according to claim 2, wherein said separators consist of conductive
20 rubber.
 5. A device according to claim 2, wherein said separators consist of conductive
polymer film.
 - 25 6. A device according to claim 2, wherein said separators consist of graphite foil.
-
7. A device according to claim 1, wherein said electrolyte is a sulphuric acid
solution.
 - 30 8. A device according to claim 1, wherein said carbonised, activated woven
fabric is formed from hydrocellulose.

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9. A device according to claim 1, wherein each said electrodes is formed of a plurality of layers of said carbonised, activated woven fabric.

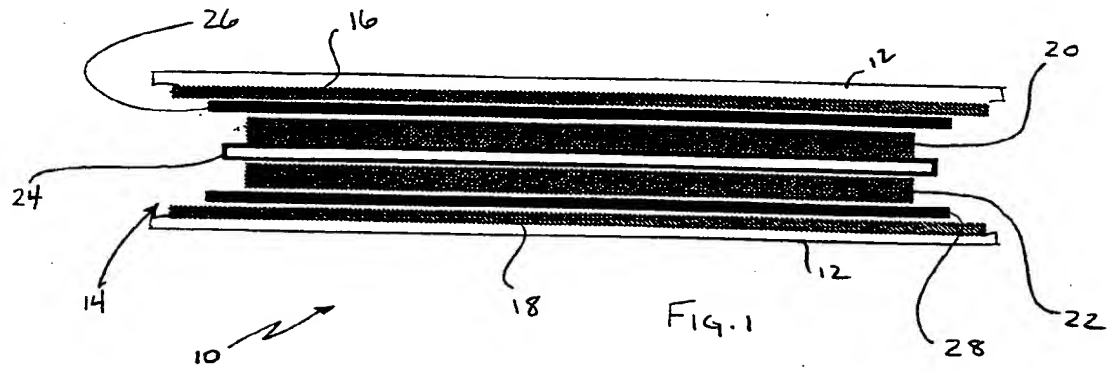
10. A device according to claim 1, wherein a single separator separates
5 neighbouring cells.

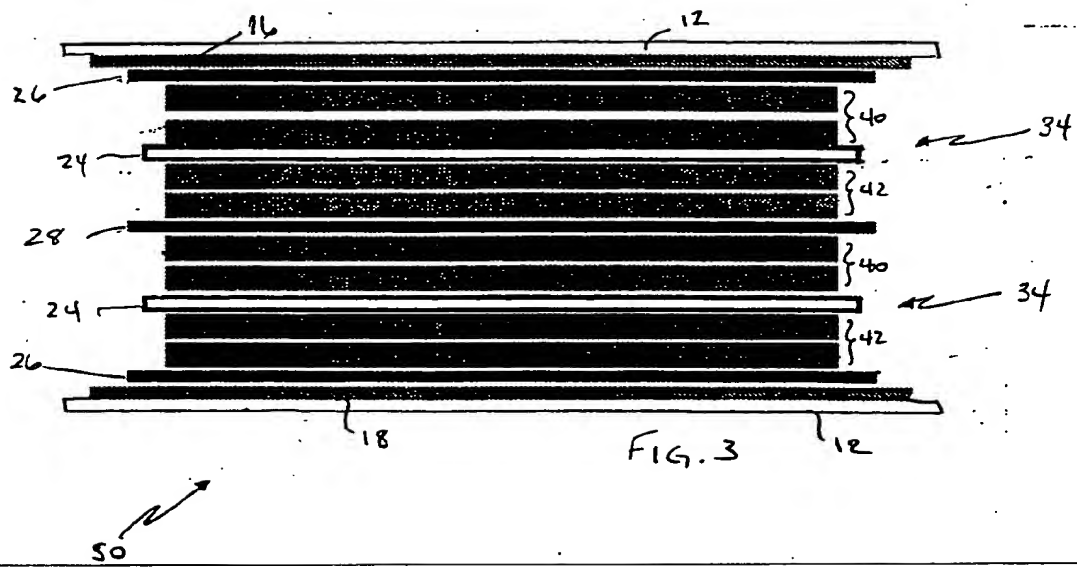
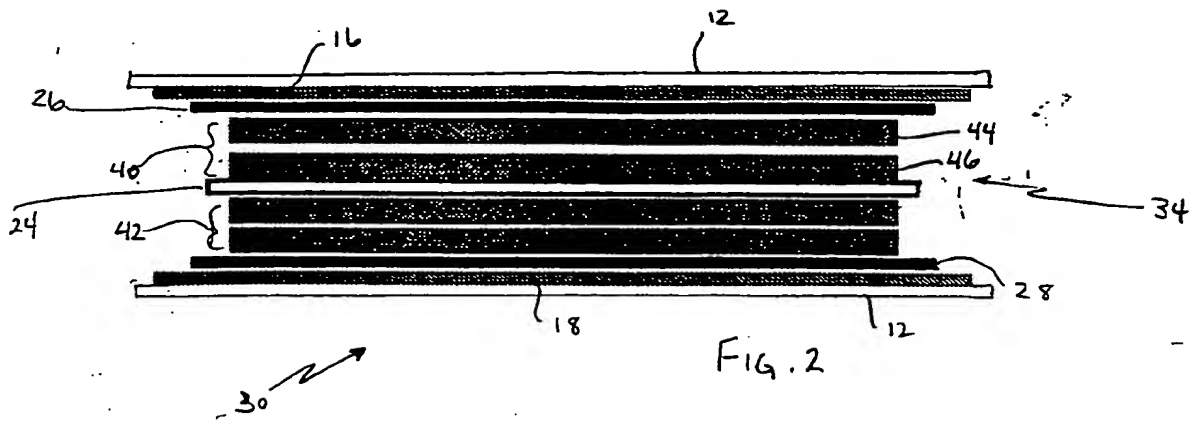
11. A capacitive cell for a high energy storage device, comprising:
a first electrode separated from a second electrode by a non-conductive,
chemically inert membrane, said electrodes formed of a carbonised, activated woven fabric
10 impregnated with an electrolyte, said chemically inert membrane permitting free passage of
molecules of said electrolyte therethrough.

12. A device according to claim 11, wherein said electrolyte is a sulphuric acid
solution.
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13. A device according to claim 11, wherein said carbonised, activated woven
fabric is formed from hydrocellulose.

14. A device according to claim 11, wherein each said electrodes is formed of a
20 plurality of layers of said carbonised, activated woven fabric.





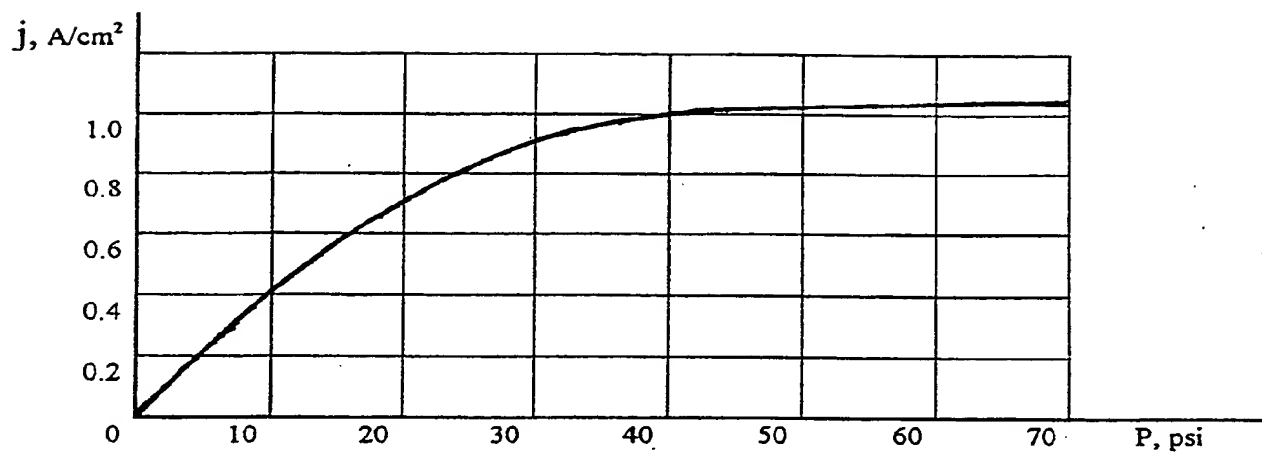


FIG. 4